Practitioner's Docket No. U 013609-7 *PATENT*

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Tsuyoshi SANO, et al
Application No.: 09/914,198 Group No.: 1755
Filed: November 13, 2001 Examiner: Callie E. Shosho
For: INK SET, METHOD OF RECORDING WITH THE SAME, AND PRINT

Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

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37 C.F.R. SECTIONS 1.52(d), 1.55(a), 1.69)

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Post Office Address 23rd Floor, Roppongi Hills Mori Tower,

6-10-1 roppongi, Minato-ku, Tokyo 106-6123 Japan

(Translation)

[Title of the Invention]	Patent Application
[Reference Number]	J0077906
[Filing Date]	April 18, 2000
[Addressed to]	Commissioner of Patent Office
[International Patent Classification]	C09D 11/00
[Inventor]	
[Address]	Seiko Epson Corporation
	3-5, Owa 3-chome, Suwa-shi, Nagano
[Name]	Kazuhide Kubota
[Applicant]	
[ID Number]	000002369
[Address]	Seiko Epson Corporation
	3-5, Owa 3-chome, Suwa-shi, Nagano
[Name]	Hideaki Yasukawa
[Applicant]	
[ID Number]	100093388
[Patent Attorney]	
[Name]	Kisaburo Suzuki
[Contact Number]	0266-52-3139
[Assigned Agent]	
[ID Number]	100095728
[Patent Attorney]	
[Name]	Masataka Ueyanagi

[Assigned Agent]

[ID Number] 100107261

[Patent Attorney]

[Name] Osamu Suzawa

[Indication of Fees]

[Advance Payment Book Number] 013044

[Amount Paid] 21,000 yen

[List of Documents Filed]

[Title] Specification 1

[Title] Abstract 1

[General Power of Attorney Number] 9711684

[Requirement of Proof] Required

[Document Name] Specification

[Title of the Invention] INK SET FOR INK JET RECORDING

[Claims]

[Claim 1]

An ink set for ink jet recording, comprising water-based pigment inks of at least six different colors, namely of black, cyan, magenta, yellow, light cyan, and light magenta, characterized in that:

each of said water-based pigment inks of said six different colors contains a pigment and a solvent;

at least said water-based inks of light cyan color and light magenta color each contains an emulsion of fine polymer particles; and

said emulsions exhibit minimum film producing temperatures of 25°C or lower.

[Claim 2]

The ink set for ink jet recording according to claim 1 characterized in that each of said water-based pigment inks of light cyan color and light magenta color contains 0.1 to 40 wt.% of said fine polymer particles.

[Claim 3]

The ink set for ink jet recording according to claim 2, characterized in that total quantity of said pigment and said fine polymer particles contained in said water-based pigment inks, respectively, is 0.5 to 45 wt.%.

[Claim 4]

The ink set for ink jet recording according to any of claims 1 to 3, characterized in that average particle size of said fine polymer particles is 5 to 200 nm.

[Claim 5]

The ink set for ink jet recording according to any of claims 1 to 4, characterized in that glass transition temperature of said fine polymer particles is –15 to 10°C.

[Claim 6]

The ink set for ink set recording according to any of claims 1 to 5, characterized in that each of said water-based pigment inks of six different colors contains a dispersant, and a content of this dispersant is 0.1 to 5 wt.%.

[Claim 7]

The water-based ink according to any of claims 1 to 6, characterized in that viscosity of each of said water-based pigment inks of six different colors at 20°C is from 1 to 10 mPa·s.

[Claim 8]

The water-based ink according to any of claims 1 to 7, characterized in that surface tension in each of said water-based pigment inks of six different colors, is 15 to 50 mN/m.

[Claim 9]

The ink set for ink jet recording according to any of claims 1 to 8, characterized in that said ink set is used in forming text and/or images on special ink jet recording paper.

[Claim 10]

A printed matter comprising text and/or images formed on said special ink jet recording paper using the ink set for ink jet recording according to any of claims 1 to 9, characterized in that, of said text and/or images, a portion

formed by using said water-based pigment ink containing said emulsion is covered with said fine polymer particles contained in said emulsion.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention relates to an ink set for ink jet recording, and more particularly relates to an ink set for ink jet recording that is capable of providing a printed matter wherein the text and/or images on a recording mediums, particularly on a special ink jet recording paper, exhibit outstanding light resistance.

[0002]

[Related Art and Problems that the Invention Intends to Solve]

For a recording medium for ink jet recording that can achieve high quality images comparable to silver chloride photographs, a special ink jet recording paper (hereinafter, simply referred to as "special paper") having an ink receiving layer has been provided. Images exhibiting a silver chloride photographic tone that are recorded on such a special paper using an ink set comprising four colors of inks, i.e., black (K), cyan (C), magenta (M) and yellow (Y), have many highlight portions wherein the ink dots are conspicuous, which has caused a problem that color images of high picture quality cannot be output.

[0003]

In order to resolve this problem, an ink set has been developed in recent years that comprises a plurality of dark and light inks that, while being mutually the same color, have different color densities. This ink set

comprises, for example, four colors of ink, namely K, C, M, and Y, that are dark ink compositions, and four colors of ink that are light inks, namely light black (Lk), light cyan (Lc), light magenta (Lm), and light yellow (Ly). An example of the ink sets comprising these dark and light inks is an ink set wherein each color ink comprises a pigment ink, and when a silver chloride photographic tone picture image is recorded on the special paper, the grainy feel caused by ink dots is diminished, which enables outputting a high quality color image comparable to silver chloride photographs.

The pigment ink has good image fastness compared to dye inks, and printed matters wherein text and/or images formed on a special paper using the pigment ink generally exhibit good light resistance.

[0004]

However, of the pigment inks, color pigment inks (i.e. C, M, Y, Lc, and Lm), but particularly the Lc color and Lm color pigment inks, do not exhibit adequate light resistance compared to the dark color inks. Therefore, in the text and/or images formed on the recording noted earlier, those portions of the recording done with such Lc color and/or Lm color ink may exhibit color fading over time, whereupon beauty may be compromised in image printings as compared to silver chloride photographs.

[0005]

Therefore, an object of the present invention is to provide an ink set for ink jet recording that is capable of providing printed matter wherein the text and/or images formed using Lc color and/or Lm color water-based pigment inks, on a recording medium, but particularly on special paper, exhibit outstanding light resistance.

[0006]

The inventors found, as a result of various investigations to achieve the object, that printed matter exhibiting outstanding text and/or image light resistance can be provided, particularly for special papers, by causing the Lc color and Lm color water-based pigment inks, respectively, to comprise fine polymer particle emulsions wherein the minimum film producing temperature is within a certain range.

[0007]

[Means for Solving the Problems]

This invention, which has as its foundation the finding noted above, is an ink set for ink jet recording, comprising water-based pigment inks of at least six colors, namely black, cyan, magenta, yellow, light cyan, and light magenta, respectively, characterized in that each of the water-based pigment inks of the six colors comprises a pigment and a solvent, in that the water-based inks of the light cyan color and the light magenta color each comprises an emulsion of fine polymer particles, and in that the emulsions exhibit minimum film producing temperatures of 25°C or lower.

[0008]

[Mode for Carrying Out the Invention]

Detailed Descriptions are given below of preferred embodiments of the ink set for ink jet recording of the present invention.

The ink set of the present invention, as described earlier, comprises water-based pigment inks of at least six colors, namely black (K), cyan (C), magenta (M), yellow (Y), light cyan (Lc) and light magenta (Lm).

The inks of K, C, M and Y above are dark inks wherein the pigments have a high concentration, and the inks of Lc and Lm are light inks wherein the pigments have a low concentration.

[0009]

These six colors of water-based pigment inks each contain a pigment and a solvent, and, at the least, the water-based pigment inks of the Lc color and the Lm color, respectively, contain an emulsion of fine polymer particles. This emulsion should have a minimum film formation temperature (MFT) of 25°C or less, preferably 0 to 25°C, and more preferably 10 to 20°C. By printing on a recording medium using an ink relating to the present invention containing an emulsion having an MFT within the ranges noted above, a protective film is automatically formed that covers the print surface at room temperature, and the light resistance of the surface of that print is enhanced. With an ink containing an emulsion wherein the MFT exceeds 25°C, on the other hand, no protective film is formed at room temperature, and separate heating means are required for forming the protective film, wherefore the light resistance of printed matter cannot be simply and easily enhanced.

Incidentally, the "emulsion" means a water-based dispersant wherein the dispersion medium is water and the dispersoid is the fine polymer particle.

The MFT is measured in accordance with JIS K 6800.

[0010]

In the emulsion noted above, to 100 parts by weight of the fine polymer particles, there should be 60 to 400 parts by weight, and preferably 100 to 200 parts by weight, of water.

[0011]

The glass transition temperature (Tg) of the fine polymer particles contained in the emulsion, in the interest of adjusting the MFT of the emulsion to within the stated ranges, should be from –15 to 10°C, and preferably from –5 to 5°C.

The Tg is measured in accordance with JIS K 6900.

Another method of adjusting the MFT of the emulsion to be within the stated ranges that may be mentioned is one using a commercially available MFT depressing agent.

[0012]

In the interest of dispersion stability in the ink, the fine polymer particles should have an average particle size of 5 to 200 nm, and preferably of 5 to 100 nm.

[0013]

It is further preferable that the fine polymer particles have a hydrophilic portion and a hydrophobic portion.

[0014]

The structure of the fine polymer particles may be either a single-phase structure or a multi-phase structure (core-shell structure). The core-shell structure may be a structure wherein two or more different polymers are present in separated phases. Examples of permissible structures include structures wherein the shell part completely covers the core part, structures wherein the shell part covers a part of the core part, structures wherein part of the polymer of the shell part forms a domain inside the polymer of the core part, structures wherein one or more other layers are between the core part

and the shell part, and multi-layer structures of three or more layers comprising layers of different compositions.

[0015]

When the core-shell structure is employed for the fine polymer particles, it is preferable that the core part thereof comprise a polymer having an epoxy group and that the shell part thereof comprise a polymer having a carboxyl group. By causing the ink to contain such fine polymer particles, the epoxy group of the core part and the carboxyl group of the shell part will form a network structure at the time of forming the protective film, thereby making it possible to enhance the strength of the protective film.

[0016]

It is also preferable that the fine polymer particles have 1 to 10 wt.% of a structure deriving from an unsaturated vinyl monomer having a carboxyl group, and 0.2 to 4 wt.% of a structure cross-linked by a cross-linking monomer that preferably has two or more but more preferably three or more double bonds capable of polymerization (i.e. a structure deriving from a cross-linking monomer). By causing the ink to contain such fine polymer particles, the nozzle plate surface will become highly resistant to wetting by that ink, curving of the flight of the liquid drops of that ink can be prevented, and discharge stability can be further improved.

[0017]

Citable examples of the unsaturated vinyl monomer having a carboxyl group as noted above include acrylic acid, methacrylic acid, itaconic acid, fumaric acid, and maleic acid, with methacrylic acid being especially preferred.

[0018]

Examples of the cross-linking monomer that may be cited include such diacrylate compounds as polyethylene glycol acrylate, triethylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,6-butylene glycol diacrylate, 1,6-hexane diol diacrylate, neopentyl glycol diacrylate, 1,9-nonane diol diacrylate, polypropylene glycol diacrylate, 2,2'-bis(4-acryloxypropyloxy-fenyl)propane, and 2,2'bis(4-acryloxydiethoxy-fenyl)propane, such triacrylate compounds as trimethylol propane triacrylate, trimethylol ethane triacrylate, and tetramethylol methane triacrylate, such tetraacrylate compounds as ditrimethylol tetraacrylate, tetramethylol methane tetraacrylate, and pentaerythritol tetraacrylate, such hexaacrylate compounds as dipentaerythritol hexaacrylate, such dimethacrylate compounds as ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butylene glycol dimethacrylate, 1,6-hexane diol dimethacrylate, neopentyl glycol dimethacrylate, dipropylene glycol dimethacrylate, polypropylene glycol dimethacrylate, polybutylene glycol dimethacrylate, and 2,2'-bis(4-methacryloxydiethoxy-phenyl)propane, and such trimethacrylate compounds as trimethylol propane methacrylate, and trimethylol ethane trimethacrylate, as well as methlene bis-acrylamide and divinyl benzene, etc.

[0019]

The fine polymer particles are caused to be contained in an ink relating to the present invention as the emulsion. However, the emulsion can be manufactured by commonly known emulsion polymerization. An emulsion of fine polymer particles can be manufactured, for example, by emulsion-polymerizing (an) unsaturated vinyl monomer(s) in water in the presence of a

surfactant (emulsifier), polymerization catalyst, polymerization starter, molecular weight adjusting agent, and neutralizing agent, etc.

[0020]

For the unsaturated vinyl monomer noted above (i.e. the monomer that configures the fine polymer particle), acrylic acid ester monomers, methacrylic acid ester monomers, aromatic vinyl monomers, vinyl ester monomers, vinyl cyanide monomers, halide monomers, olefin monomers, and diene monomers and the like that are commonly used in emulsification polymerization may be used. These include, more specifically, such acrylic acid esters as methyl acrylate, ethyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, n-amyl acrylate, isoamyl acrylate, n-hexyl acrylate, 2-ethylhexyl acrylate, octyl acrylate, decyl acrylate, dodecyl acrylate, octadecyl acrylate, cyclohexyl acrylate, phenyl acrylate, benzyl acrylate, and glycidyl acrylate, such methacrylic acid esters as methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, n-amyl methacrylate, isoamyl methacrylate, n-hexyl methacrylate, 2-ethylhexyl methacrylate, octyl methacrylate, decyl methacrylate, dodecyl methacrylate, octadecyl methacrylate, cyclohexyl methacrylate, phenyl methacrylate, benzyl methacrylate, and glycidyl methacrylate, such vinyl esters as vinyl acetate, such vinyl cyanides as acrylonitrile, such halogenated monomers as vinylidene chloride and vinyl chloride, such aromatic vinyl monomers as styrene, 2-methyl styrene vinyl toluene, tert-butyl styrene, chlorostyrene, anisole vinyl, and vinyl naphthalene, such olefins as ethylene, propylene, and isopropylene, such dienes as butadiene and chloroprene, and such vinyl monomers as vinyl ether, vinyl ketone, and vinyl pyrrolidone, etc.

[0021]

Examples of the surfactant that may be cited include anionic surfactants (sodium dodecyl benzene sulfonate salts, sodium laurate salts, and polyoxyethylene alkyl ether sulfate ammonium salts), and non-ionic surfactants (polyoxyethylene alkyl ethers, polyoxyethylene alkyl esters, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene alkyl phenyl ethers, polyoxyethylene alkyl amines, and polyoxyethylene alkyl amides), one type or two or more types whereof can be used. Acetylene glycol (Olefin Y, and surfynol 82, 104, 440, 465, and 485 (all made by Air Products and Chemicals Inc.)) can also be used.

[0022]

When manufacturing the emulsion (the fine polymer particles), in the interest of enhancing print stability, during the emulsification polymerization noted earlier, it is preferable that, in addition to the unsaturated vinyl monomer, either one type or two or more types selected from a group made up of acrylamides and monomers having a hydroxyl group also be mixed in. Citable examples of such acrylamides include acrylamide and N,N'-dimethyl acrylamides, one type or two or more types whereof can be used when such are used. Citable examples of such monomers having a hydroxyl group, moreover, include 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, and 2-hydroxypropyl methacrylate, one or two or more types whereof can be used.

[0023]

Furthermore, when the fine polymer particles used are those having the core-shell structure noted earlier, the resin emulsion containing those can be manufactured, for example, by the method disclosed in Japanese Patent

Application Laid-Open No. H4-76004/1992 (published) (multi-stage emulsification polymerization of the unsaturated vinyl monomers noted earlier).

Also, as noted earlier, fine polymer particles having the core-shell structure should preferably have a core part comprising a polymer having an epoxy group. For the method of introducing the epoxy group into the core part, there are, for example, the method of copolymerizing a glycidyl acrylate, glycidyl methacrylate, or allyl glycidyl ether or the like, that is an unsaturated vinyl monomer having an epoxy group, with another unsaturated vinyl monomer, and the method of polymerizing one or more types of unsaturated vinyl monomers to prepare the core part (core particle), adding an epoxy compound simultaneously, and making those into a complex. The former of these two methods is preferable in the interest of ease of polymerization and of polymerization stability.

[0024]

The amount of fine polymer particles that should be contained respectively in the Lc color and the Lm color water-based pigment inks relating to the present invention should be from 0.1 to 40 wt.%, and preferably from 0.5 to 20 wt.%.

In particular, the total amount of the pigment and the fine polymer particles contained in those Lc color and Lm color water-based pigment inks, respectively, should be from 0.5 to 45 wt.%, and preferably from 1 to 25 wt.%.

When the amount of fine polymer particles contained in the Lc color and the Lm color water-based pigment inks is less than 0.1 wt.%, it is not possible to adequately cover the text and/or images formed on the recording medium using these inks with a protective film (described further below), and

color fading in those text and/or images cannot be effectively prevented. When the amount thereof contained exceeds 40 wt.%, on the other hand, troubles arise such as nozzle clogging or ink discharge instability.

[0025]

For the pigments noted in the foregoing, relating to the ink set for ink jet recording of the present invention, the same pigments as are commonly used in this type of ink are used, as, for example, such organic pigments as azo lake, insoluble azo pigment, condensed azo pigment, chelated azo pigment, phthalocyanine pigment, perylene pigment, perinone pigment, quinacridone pigment, thio-indigo pigment, isoindolinone pigment, quinophthalone pigment, dioxazine pigment, anthraquinone pigment, nitro pigment, nitroso pigment, and aniline black, etc., and such inorganic pigments as titanium white, flowers of zinc, lead white, carbon blacks, iron oxide red, cinnabar, cadmium red, yellow lead, ultramarine, cobalt blue, cobalt violet, and zinc chromate, etc. Also, any pigment can be used, even one that is not listed in the color index, so long as it can disperse in the water phase. By "pigment," furthermore, is meant a particle-form solid that is insoluble in water, solvents, and oils, etc.

[0026]

In the interest of enhancing ink storage stability and preventing nozzle clogging, moreover, the average particle size of the pigment should be 20 to 200 nm, and preferably 50 to 100 nm.

[0027]

In the dark inks relating to the present invention, the pigment content should be from 0.5 to 25 wt.%, and preferably from 2 to 15 wt.%. When the pigment content is less than 0.5 wt.%, the print and image density is

inadequate for a dark ink, whereas, when the content thereof exceeds 25 wt.%, no great improvement in print or image density is gained, but problems arise such as a decline in ink liquid stability.

From the same perspective, moreover, it is preferable that, in the light inks relating to the present invention, the pigment be contained at a concentration of from 1/10 to 1/2 the pigment concentration in the dark inks, and more preferable that that range be from 1/10 to 1/4.

[0028]

For the solvent relating to the ink set for ink jet recording of the present invention, water is used, preferably ion-exchange water.

[0029]

In addition to water, moreover, an organic solvent may also be jointly used for the solvent. Such an organic solvent should be miscible with water, enhance ink permeability into the recording medium and aid in preventing nozzle clogging, and also enhance the solubility of the various components mixed into the ink. Examples are alkylalcohols having 1 to 4 carbons such as ethanol, methanol, butanol, propanol, isopropanol, glycol ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol monomethyl ether acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-propyl ether, ethylene glycol mono-iso-propyl ether, diethylene glycol mono-iso-propyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-t-butyl ether, diethylene glycol mono-t-butyl ether, 1-methyl-1-methoxy butanol, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-t-butyl ether, propylene glycol mono-n-propyl ether,

propylene glycol mono-iso-propyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol mono-n-propyl ether, dipropylene glycolmono-iso-propyl ether, formamide, acetamide, dimethyl sulfoxide, sorbit, sorbitan, acetin, diacetin, triacetin, sulfolane, one or two or more types whereof can be used.

[0030]

The solvent noted above should be contained in an ink relating to the present invention in a quantity of from 0.5 to 40 wt.%, and preferably from 2 to 20 wt.%.

[0031]

The ink set for ink jet recording of the present invention is made, by having the fine polymer particles noted earlier contained in the Lc color and the Lm color inks, respectively, that are light inks, so as to be capable of easily and simply forming text and/or images exhibiting outstanding light resistance on recording mediums, especially on special papers. As necessary, the light resistance thereof can be further enhanced by mixing a light resistance enhancer into the Lc color and Lm color inks, respectively.

Such a light resistance enhancer need only be water soluble and capable of preventing color fading, spoiling, and aging and the like caused by UV light and visible light, preferably being one type or two or more types selected from among a group made up of UV absorbers, light stabilizers, light blockers, and antioxidants. A UV absorber is particularly desirable.

[0032]

Citable examples of the UV absorbers include benzophenone systems, salicylate systems, benzotriazol systems, and cyanoacrylate systems, as well

as such metal oxides as titanium oxide, zinc oxide, selenium oxide, and cerium oxide, etc. Citable examples of the light stabilizers include hindered amine based light stabilizers (HALS). Citable examples of the light blockers include nickel salts such as nickel dibutyldithiocarbamate, nickel sulfate, and nickel oxalate, and such metal halide salts as potassium iodide, sodium iodide, potassium bromide, sodium bromide, and potassium chloride, together with potassium thiocyanate, cobalt sulfate, copper sulfate, and ferrous sulfate, etc. And citable examples of the antioxidants include hindered phenol compounds, amine compounds, phosphorous compounds, and sulfur compounds.

[0033]

In the inks relating to the present invention, furthermore, in the interest of enhancing text and/or image wear resistance, a water-based emulsion of a thermoplastic resin can be mixed in. Such a thermoplastic resin should be one that is insoluble in water and that forms a film exhibiting outstanding adhesion and wear resistance when heated to or above the softening temperature or melting temperature and then cooled. Specific examples that may be cited include polyacrylic acids, polymethacrylic acids, polymethacrylic acid esters, polyethyl acrylic acids, styrene-butadiene copolymers, polybutadiene, acrylonitrile butadiene copolymers, chloroprene copolymers, fluorine resins, vinylidene chloride, polyolefin resins, cellulose, styrene-acrylic acid copolymers, styrene-methacrylic acid copolymers, polystyrenes, styrene-acrylamide copolymers, polyisobutyl acrylates, polyacrylonitriles, polyvinyl acetates, polyvinyl acetals, polyamides, rosin resins, polystyrenes, polycarbonates, vinylidene chloride resins, cellulose resins, vinyl acetate resins, ehylene-vinyl acetate copolymers, vinyl acetate-acrylic acid

copolymers, vinyl chloride resins, polyurethanes, and rosin esters. Specific examples of such thermoplastic resins that are of low molecular weight that may be cited include such animal- or plant-based waxes as polyethylene waxes, montan wax, alcohol waxes, synthetic oxide waxes, α-olefin-anhydrous maleic-acid copolymers, and carnauba wax, as well as lanolin, paraffin waxes, and microcrystalline waxes, etc.

[0034]

Also, for the water-based emulsion of a thermoplastic resin noted above, those described in Japanese Patent Publication No. S62-1426, Japanese Patent Application Laid-Open No. H3-56573, Japanese Patent Application Laid-Open No. H3-796178, Japanese Patent Application Laid-Open No. H3-160068, and Japanese Patent Application Laid-Open No. H4-18462, for example, can be used.

[0035]

In the inks relating to the present invention, furthermore, in the interest of enhancing pigment dispersion stability, a dispersant can be mixed in. For such a dispersant, for example, a dispersant commonly used in preparing pigment dispersions, such as a polymer dispersant or a surfactant, can be used. Such a polymer dispersant may be either a natural polymer or a synthetic polymer. For such a surfactant, one like that used in manufacturing the emulsion noted earlier may be used.

[0036]

Citable examples of the natural polymers, which are among the polymer dispersants, include such proteins as animal glue, gelatin, casein, and albumin, such natural rubbers as gum arabic and gum tragacanth, such

glycosides as saponin, alginic acid and such alginic acid derivatives as alginic acid propylene glycol esters, triethanolamine alginate, and ammonium alginate, and such cellulose derivatives as methyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, and ethylhydroxy cellulose.

[0037]

Citable examples of synthetic polymers, which are among the polymer dispersants, include such acrylic resins as polyvinyl alcohols, polyvinyl pyrrolidones, polyacryl acids, copolymers of acrylic acid and acrylonitrile, copolymers of potassium acrylate and acrylonitrile, copolymers of vinyl acetate and acrylic acid esters, and copolymers of acrylic acid and acrylic acid esters, such styrene-acrylic resins as styrene-acrylic acid copolymers, styrene-methacrylic acid copolymers, styrene-methacrylic acid-acrylic acid ester copolymers, styrene-α-methylstyrene-acrylic acid copolymers, and styrene-α-methylstyrene-acrylic acid-acrylic acid ester copolymers, and such vinyl acetate copolymers as styrene-maleic acid copolymers, styrene-anhydrous maleic acid copolymers, vinyl naphthalene-acrylic acid copolymers, vinyl naphthalene-maleic acid copolymers, vinyl acetate-ethylene copolymers, vinyl acetate-fatty acid vinyl ethylene copolymers, vinyl acetate-maleic acid ester copolymers, vinyl acetate-crotonic acid copolymers, and vinyl acetate-acrylic acid copolymers, together with salts thereof. In particular, a copolymer consisting of a monomer having a hydrophobic group and a monomer having a hydrophilic group, and a polymer consisting of a monomer having both a hydrophobic group and a hydrophilic group in the molecular structure, are to be preferred.

[0038]

The amount of such dispersant contained in an ink relating to the present invention should be from 0.2 to 15 wt.%, and preferably from 1 to 10 wt.%.

[0039]

In the inks relating to the present invention, moreover, in the interest of enhancing print quality, an acetylene glycol based surfactant can be mixed in. Citable examples of such acetylene glycol surfactants include 2,4,7,9-tetramethyl-5-decine-4,7-diol, 3,6-dimethyl-4-octene-3,6-diol, 3,5-dimethyl-1-hexene-3-ol, used either singly or in combinations of two or more types.

The amount of such an acetylene glycol surfactant contained in an ink relating to the present invention should be from 0.1 to 5 wt.%, and preferably from 0.1 to 2 wt.%.

[0040]

In the inks relating to the present invention, furthermore, in the interest of preventing nozzle clogging, a water soluble glycol can be mixed in. Citable examples of such water soluble glycols include ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, polyethylene glycols having a molecular weight of 2000 or lower, 1,3-propylene glycol, isopropylene glycol, isobutylene glycol, 1,4-butane diol, 1,3-butane diol, 1,5-pentane diol, 1,6-hexane diol, glycerin, mesoerythritol, and pentaerythritol, which can be used either singly or in combinations of two or more types.

The amount of such water soluble glycol contained in an ink relating to the present invention should be from 0.5 to 40 wt.%, and preferably from 2 to 20 wt.%.

[0041]

Similarly, in the interest of preventing nozzle clogging, a saccharide can be mixed into an ink relating to the present invention. Examples of such saccharides that may be cited include glucose, mannose, fructose, ribose, xylose, arabinose, lactose, galactose, aldonic acids, glucitose, maltose, cellobiose, sucrose, trehalose, maltotriose, alginic acid and salts thereof, cyclodextrins, and celluloses, which can be used singly or in combinations of two or more types.

The amount of such saccharide contained in an ink relating to the present invention should be from 0.5 to 40 wt.%, and preferably from 2 to 20 wt.%.

[0042]

Similarly, in the interest of preventing nozzle clogging, a mildew retardant or preservative can be mixed into the inks relating to the present invention. Citable examples of such mildew retardants or preservatives include sodium benzoate, sodium pentachlorophenol, sodium 2-pyridine thiol-1-oxide, sodium sorbinate, sodium dehydroacetate, and 1,2-benzisothiazolin-3-one (such as Proxel CRL, Proxel BDN, Proxel GXL, Proxel XL-2, and Proxel TN, made by ICI), which can be used either singly or in combinations of two or more types.

The amount of such mildew retardant or preservative contained in an ink relating to the present invention should be from 0.01 to 2 wt.%, and preferably from 0.1 to 1 wt.%.

[0043]

In addition, as necessary, the inks relating to the present invention can be made to contain such additives as viscosity adjusters, surface tension adjusters, pH adjusters, antifoaming agents, chelating agents, and oxygen absorbers, which can be used singly or in combinations of two or more types.

[0044]

In the interest both of easily forming the protective film noted earlier, having a prescribed thickness, and of improving discharge stability, it is desirable that the viscosities of the inks relating to the present invention, respectively, be from 1 to 10 mPa·s, with a range of 2 to 5 mPa·s being particularly desirable. In order to bring the viscosity within those ranges, for the viscosity adjuster noted above, a rosin, alginic acid, polyvinyl alcohol, hydroxypropyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, methyl cellulose, polyacrylate, polyvinyl pyrrolidone, or gum arabic starch or the like can be added.

[0045]

In the interest of enhancing discharge stability, it is desirable that the surface tension of the inks relating to the present invention be made from 15 to 50 mN/m, and preferably from 25 to 40 mN/m.

The surface tension is measured in accordance with JIS K 3211.

[0046]

In the interest of enhancing print density and of liquid stability, the pH of the inks relating to the present invention, respectively, should be made from 7 to 11, and preferably from 8 to 10.

In order to bring the pH to within those ranges, monoethanolamine or triaminoethanol or the like can be added as the pH adjuster noted earlier.

[0047]

The ink set for ink jet recording of the present invention, in like manner as this type of ink set, can be mounted in an ink jet recording apparatus (ink jet printer) and can form text and/or images on a recording medium such as special paper. When such is done, at the portions of the text and/or images formed using the Lc color and/or the Lm color water-based pigment ink, at room temperature, a protective film is formed, based on a polymer configuring the fine polymer particles described earlier, which covers those portions. As a consequence, the light resistance of those portions is enhanced, and color fading or disappearance or the like over time in those portions due to UV light or visible light is prevented. Also, that protective film causes pigment in the ink to adhere strongly to the recording medium surface, wherefore the wear resistance and light resistance of those portions are also improved. Also, that protective film is formed automatically, without the use of any special heating means, immediately after the text and/or images are formed, wherefore printed matter light resistance can be easily and simply improved.

[0048]

The ink set for ink jet recording of the present invention can be used compatibly with a recording medium that is either plain paper or special paper, but is particularly effective on special paper. By "plain paper" here is meant paper such as paper for PPC (plain paper copier) use in which no consideration has been given to the characteristics of ink jet recording.

As to special paper, there are two types, namely the "swelling type" which comprises a water soluble resin such as a polyvinyl alcohol in the ink accepting layer thereof, and the "absorbing type" which comprises a porous

material such as amorphous silica in the ink accepting layer. The ink set for ink jet recording of the present invention can be used compatibly with either type of special paper, but, from the perspective of the printed matter being quick-drying, the absorbing type special paper is particularly to be preferred.

[0049]

When the ink set for ink jet recording of the present invention is used to form text and/or images on such special paper, the pigments and fine polymer particles in the inks will respectively collect near the surface of such special paper, wherefore printed mater exhibiting high coloring is obtained, and the protective film covering those text and/or images will be formed stably, wherefore printed matter light resistance can be easily and simply enhanced.

[0050]

The ink set for ink jet recording of the present invention is not limited to that embodiment.

The ink set for ink jet recording of the present invention, for example, need only comprise water-based pigment inks in at least the six colors of B, C, M, Y, Lc, and Lm, and may be an ink set comprising seven colors of water-based pigment inks, or an ink set comprising eight colors of water-based pigment inks.

When the ink set is made to have seven colors, it is preferable that dark inks be comprised in the colors K, C, M, Y, and dark yellow (DY), respectively, and that light inks be comprised in the colors Lc and Lm, respectively.

And when the ink set is made to have eight colors, it is preferable that dark inks be comprised in the colors K, C, M, Y, and DY, respectively, and that light inks be comprised in the colors Lk, Lc and Lm, respectively.

[0051]

Also, it is only necessary that the fine polymer particles relating to the present invention be contained at least in the Lc color and the Lm color water-based pigment inks, respectively, and they may be made to be contained in water-based pigment inks of other colors. In such cases, the amounts of those fine polymer particles contained in the water-based pigment inks of colors other than the Lc color and the Lm color should, respectively, be from 0.1 to 40 wt.%, but preferably from 0.5 to 20 wt.%.

[0052]

[Embodiments]

Embodiments of the water-based ink of the present invention are described below. However, needless to say, the present invention is in no way limited by these embodiments. Unless otherwise noted, moreover "parts" and "%" indicate parts by weight and "wt.%," respectively.

[0053]

[Preparation of Emulsion A]

Into a flask equipped with a stirring apparatus, thermometer, recirculating cooler, and drip funnel were placed 100 ml of distilled water and 0.1 g of potassium persulfate. The contents of the flask were heated, while stirring under a nitrogen atmosphere, until the temperature thereof reached 70°C. Separately, an emulsion was prepared by placing 100 ml of distilled water, 1.0 g of sodium dodecylbenzene sulfonate, 30 g of styrene, 55 g of 2-

ethylhexyl acrylate, and 5 g of methacrylic acid into a reaction vessel and stirring. Then, using the drip funnel, that emulsion was slowly dripped into the flask, thus preparing an emulsion having fine polymer particles as the dispersoid. After cooling this emulsion to room temperature, it was filtered through a 0.4 μm filter, and then distilled water was added to make the concentration of the fine polymer particles 30%, thus yielding emulsion A. The MFT of this emulsion A was 20°C.

[0054]

[Preparation of Emulsion B]

Except in that an emulsion prepared from [100 ml distilled water, 1.0 g sodium dodecylbenzene sulfonate, 50 g styrene, 35 g 2-ethylhexyl acrylate, and 5 g methacrylic acid] was used instead of the emulsion described in the foregoing [Preparation of Emulsion A], an emulsion B was obtained that was prepared in the same manner as described in the foregoing [Preparation of Emulsion A]. The MFT of the emulsion B was 60°C.

[0055]

[Preparation of Water-Based Pigment Ink]

Pigment, dispersant, and water were placed in a vessel and a mixture was prepared. Then glass beads (1.7 mm in diameter) were added in a quantity (by weight) 1.5 times that of the mixture, and dispersing was conducted for two hours using a sand mill (made by Yasukawa Seisakujo). Then the glass beads were removed and a pigment dispersion was prepared. Meanwhile, the ink components (organic solvent, etc.) other than the pigment and dispersant noted above were placed in a separate vessel and mixed to prepare an ink solvent. Then, while stirring the pigment dispersion, the ink

solvent was slowly dripped in, and, after stirring for 20 minutes at room temperature, this was filtered through a 5 μm membrane filter to yield a water-based pigment ink.

[0056]

[Embodiment 1]

According to [Preparation of Water-Based Pigment Ink] above, six colors of water-based pigment inks were severally prepared, and an ink set 1 comprising each of those six colors of water-based pigment inks was obtained. Also, emulsion A obtained according to [Preparation of Emulsion A] above was mixed into the Lc color and Lm color inks, respectively, of those six colors of water-based pigment inks. The compositions of the various colors of ink were as noted below, respectively.

[0057]

<Black ink 1 composition>

Carbon black MA7 (Mitsubishi Chemical Corporation)	5.0%
Styrene-acrylic acid copolymer (dispersant)	1.0%
Glycerin	10.0%
Ion exchange water	Balance
Total	100%

[0058]

<Cyan ink 1 composition>

C.I. pigment blue 15:3	2.0%
Styrene-acrylic acid copolymer (dispersant)	1.0%
Diethylene glycol	10.0%
Ion exchange water	balance

Total	100%

[0059]

<Magenta ink 1 composition>

C.I. pigment red 122	3.0%
Styrene-acrylic acid copolymer (dispersant)	1.0%
Glycerin	5.0%
Diethylene glycol	5.0%
Ion exchange water	balance
Total	100%

[0060]

<Yellow ink 1 composition>

C.I. pigment yellow 74	3.5%
Styrene-acrylic acid copolymer (dispersant)	1.0%
Glycerin	8.0%
Ion exchange water	balance
Total	100%

[0061]

<Light cyan ink 1 composition>

C.I. pigment blue 15:3	0.5%
Styrene-acrylic acid copolymer (dispersant)	1.0%
Emulsion A (as fine polymer particle concentration)	0.1%
Diethylene glycol	10.0%
Ion exchange water	balance
Total	100%

[0062]

<Light magenta ink 1 composition>

C.I. pigment red 122	0.6%
Styrene-acrylic acid copolymer (dispersant)	1.0%
Emulsion A (as fine polymer particle concentration)	0.1%
Glycerin	5.0%
Diethylene glycol	5.0%
Ion exchange water	balance
Total	100%

[0063]

[Embodiment 2]

Except in that the ink compositions noted below were used instead of the ink compositions of the various inks in [Embodiment 1] above, respectively, an ink set E was obtained which comprised water-based pigment inks in six colors, respectively, as in [Embodiment 1] described above.

[0064]

<Black ink 2 composition>

C.I. pigment black 1	1.0%
Styrene-acrylic acid copolymer (dispersant)	1.0%
Glycerin	15.0%
Ion exchange water	balance
Total	100%

[0065]

<Cyan ink 2 composition>

C.I. pigment blue 15:3	2.0%
Styrene-acrylic acid copolymer (dispersant)	1.0%

Diethylene glycol		10.0%
Ion exchange water		balance
	Total	100%

[0066]

<Magenta ink 2 composition>

C.I. pigment red 122	3.0%
Styrene-acrylic acid copolymer (dispersant)	1.0%
Glycerin	5.0%
Diethylene glycol	5.0%
Ion exchange water	balance
Total	100%

[0067]

<Yellow ink 2 composition>

C.I. pigment yellow 74	3.5%
Styrene-acrylic acid copolymer (dispersant)	1.0%
Glycerin	8.0%
Ion exchange water	balance
Total	100%

[0068]

<Light magenta 2 composition>

C.I. pigment blue 15:3	0.5%
Styrene-acrylic acid copolymer (dispersant)	1.0%
Emulsion A (as fine polymer particle concentration)	3.0%
Diethylene glycol	10.0%
Ion exchange water	balance

Total	100%

[0069]

<Light magenta 2 composition>

C.I. pigment red 122	0.6%
Styrene-acrylic acid copolymer (dispersant)	1.0%
Emulsion A (as fine polymer particle concentration)	3.0%
Glycerin	5.0%
Diethylene glycol	5.0%
Ion exchange water	balance
Total	100%

[0070]

[Comparative Example 1]

Except in that emulsion B obtained by [Preparation of Emulsion B] above was mixed into the Lc color and Lm color inks, instead of emulsion A in [Embodiment 2] above, an ink set 3 was obtained comprising water-based pigment inks in six colors, respectively, as in [Embodiment 2] described earlier. The compositions of the various inks were as noted below, respectively.

[0071]

<Black ink 3 composition>

C.I. pigment black 1	1.0%
Styrene-acrylic acid copolymer (dispersant)	1.0%
Glycerin	15.0%
Ion exchange water	balance
Total	100%

[0072]

<Cyan ink 3 composition>

C.I. pigment blue 15:3	2.0%
Styrene-acrylic acid copolymer (dispersant)	1.0%
Diethylene glycol	10.0%
Ion exchange water	balance
Total	100%

[0073]

<Magenta ink 3 composition>

C.I. pigment red 122	3.0%
Styrene-acrylic acid copolymer (dispersant)	1.0%
Glycerin	5.0%
Diethylene glycol	5.0%
Ion exchange water	balance
Total	100%

[0074]

<Yellow ink 3 composition>

C.I. pigment yellow 74	3.5%
Styrene-acrylic acid copolymer (dispersant)	1.0%
Glycerin	8.0%
Ion exchange water	balance
Total	100%

[0075]

<Light cyan ink 3 composition>

C.I. pigment blue 15:3	0.5%
Styrene-acrylic acid copolymer (dispersant)	1.0%

Emulsion B (as fine polymer particle concentration)	3.0%
Diethylene glycol	10.0%
Ion exchange water	balance
Total	100%

[0076]

<Light magenta ink 3 composition>

C.I. pigment red 122	0.6%
Styrene-acrylic acid copolymer (dispersant)	1.0%
Emulsion B (as fine polymer particle concentration)	3.0%
Glycerin	5.0%
Diethylene glycol	5.0%
Ion exchange water	balance
Total	100%

[0077]

[Comparative Example 2]

Except in that the ink compositions noted below were used instead of the ink compositions of the various inks in [Embodiment 1] above, respectively, an ink set 4 was obtained which comprised water-based pigment inks in six colors, respectively, as [Embodiment 1] above. The compositions of the various colors of inks were as noted below, respectively.

[0078]

<Black ink 4 composition>

Carbon black MA7 (Mitsubishi Chemical Corporation)	5.0%
Styrene-acrylic acid copolymer (dispersant)	1.0%
Glycerin	10.0%

Ion exchange water	balance
Total	100%

[0079]

<Cyan ink 4 composition>

Pigment KETBLUEEX-1	2.0%
(made by Dainippon Ink and Chemicals Inc.)	
Styrene-acrylic acid copolymer (dispersant)	1.0%
Glycerin	10.0%
Ion exchange water	balance
Total	100%

[0080]

<Magenta ink 4 composition>

Pigment KET Red 309	3.0%
(made by Dainippon Ink and Chemicals Inc.)	
Styrene-acrylic acid copolymer (dispersant)	1.0%
Diethylene glycol	5.0%
Ion exchange water	balance
Total	100%

[0081]

<Yellow ink 4 composition>

Pigment KET Yellow 403	3.0%
(made by Dainippon Ink and Chemicals Inc.)	
Styrene-acrylic acid copolymer (dispersant)	1.0%
Ethylene glycol	8.0%
Ion exchange water	balance

Total	100%

[0082]

<Light cyan ink 4 composition>

Pigment KETBLUEEX-1	0.6%
(made by Dainippon Ink and Chemicals Inc.)	
Styrene-acrylic acid copolymer (dispersant)	1.0%
Glycerin	10.0%
Ion exchange water	balance
Total	100%

[0083]

<Light magenta ink 4 composition>

Pigment KET Red 309	0.8%
(made by Dainippon Ink and Chemicals Inc.)	
Styrene-acrylic acid copolymer (dispersant)	1.0%
Diethylene glycol	15.0%
Ion exchange water	balance
Total	100%

[0084]

(Light Resistance Evaluation)

Using the ink sets of Embodiments 1 and 2 (ink sets 1 and 2) and of Comparative Examples 1 and 2 (ink sets 3 and 4), images were formed on recording media, which were then evaluated according to the "Light Resistance Evaluation Criteria" noted below. The results of those evaluations are given in Table 1.

[0085]

(Light Resistance Evaluation Criteria)

Using ink jet printers (model "PM-770C" made by Seiko Epson (KK)) into which the ink sets 1 to 4, respectively, had been loaded, images were formed on special ink jet recording medium (product name "Photoprint Paper 2," made by Seiko Epson), in an environment at a temperature of 25°C, yielding printed materials.

Those printed materials, respectively, were placed under glass and subjected to direct sunlight exposure for one month in an environment at a temperature of 25°C. Then, for the portions of the images formed thereon having an inked volume constituting a 30% duty, the color phases before and after the direct sunlight exposure treatment were measured respectively with a CE-7000 spectrophotometer (made by Macbeth), and coordinates in the L*a*b colorimetric system in the color difference representation method defined by the CIE were found. The color differences (ΔE) of the images before and after the direct sunlight exposure treatment were found by the following formula, and evaluated according to the following evaluation criteria.

$$\Delta E = \{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2\}^{1/2}$$

(evaluation criteria)

A: ΔE is less than 2.

B: ΔE is 2 or greater but less than 3.

C: ΔE is 3 or greater but less than 4.

D: ΔE is 4 or greater but less than 5.

E: ΔE is 5 or greater.

[0086]

Table 1

		Emulsion		Light Resistance
		Content (%)	MFT(°C)	
Embodiments	1	0.1	20 *1	B
	2	3	20 *1	A
Comparative Examples	1	3	60 *2	C
	2	-	-	E

*1: Emulsion A

*2: Emulsion B

[0087]

As is clear from the results given in Table 1, all of the materials printed using the ink sets of Embodiment 1 and Embodiment 2 exhibited outstanding light resistance. In all of the materials printed using the ink sets of Comparative Example 1 and Comparative Example 2, on the other hand, it is evident that light resistance is inferior.

In the ink set in Comparative Example 1, because the MFT of the emulsion B mixed into the light inks (i.e. the Lc color and Lm color inks), namely 60°C, is higher than room temperature (25°C), in the recording portions recorded on the special paper with those light inks, the protective film for covering those recorded portions was not adequately formed. As a consequence, color fading and the like could not be adequately prevented in those recorded portions.

In the ink set in Comparative Example 2, moreover, because no emulsion is mixed into either of those two colors of light inks, light resistance in the printed material is markedly inferior.

[0088]

As noted earlier, light-induced color fading occurs more readily in the Lc color and Lm color inks which are light inks than in dark inks. That being so, if an emulsion exhibiting a film forming property is included in those light inks, it becomes possible to protect the text and/or images formed by those light inks and to enhance the light resistance thereof. When that was done, the light resistance of the text and/or images formed respectively by the dark and light inks became roughly the same level, respectively, and it became possible to maintain a balance in color fading therein. In particular, by using an emulsion exhibiting a film forming property with an MFT of 25°C or lower, a film for protecting the text and/or images formed by the light inks is adequately formed, wherefore the light resistance thereof markedly increases. When printing was performed using ink sets of the present invention comprising such dark and light inks as these (Embodiments 1 and 2), the balance in light-induced color fading in the text and/or images was good, and variation in the color phase (ΔE) was diminished.

[0089]

[Effects of the Invention]

Based on the ink sets for ink jet recording of the present invention, moreover, the light resistance of text and/or images formed using an Lc color and/or Lm color water-based pigment ink, particularly on special paper, can be enhanced, and printed matter can be provided that exhibits outstanding light resistance.

Based on the ink sets for ink jet recording of the present invention, moreover, a protective film for covering text and/or images formed on special paper by the Lc color and/or the Lm color water-based pigment inks can be

formed without using any special heating means, wherefore printed matter exhibiting outstanding light resistance can be easily and simply provided.

[Title of Document] Abstract

[Abstract]

[Object] To provide an ink set for ink jet recording that is capable of providing printed matter comprising text and/or images, formed on a recording medium, particularly on special paper, that exhibits outstanding light resistance.

[Solution] An ink set for ink jet recording, comprising water-based pigment inks of at least six different colors, namely of black, cyan, magenta, yellow, light cyan, and light magenta, characterized in that: each of said water-based pigment inks of said six different colors contains a pigment and a solvent; at least said water-based inks of light cyan color and light magenta color each contains an emulsion of fine polymer particles; and said emulsions exhibit minimum film producing temperatures of 25°C or lower, is provided.

[Selected Drawing] None